Environment-Friendly Chemical Recycling of Aliphatic Polyurethanes by Hydrolysis in a CO$_2$-Water System

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Abstract

In order to develop a chemical recycling system of polyurethanes (PUs), environment-friendly hydrolysis of two types of aliphatic PUs was studied under pressured CO_2 in water, in which the carbonic acid generated from CO_2 acted as an acid catalyst. Two PUs, namely H-PU or I-PU, were synthesized starting from 1,4-butanediol and 1,6-hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI), respectively. The hydrolysis of PUs depended on the experimental conditions, such as the temperature and CO_2 pressure. As a result, 98% of H-PU and 91% of I-PU were successfully hydrolyzed under the typical conditions of 190 °C for 24 h at 8.0 MPa CO_2.

The reaction mixtures afforded 1,4-butanediol and diamines without the formation of any byproducts. Both of these raw materials generated from the originated PUs by selective hydrolytic cleavage of the urethane linkages, and they were easily isolated in high yields simply by evaporation of the water-soluble components within the reaction mixture. By comparing the results of the two aliphatic PUs with those of an aromatic PU (M-PU), the hydrolyzability was found to decrease in the order H-PU, I-PU, and M-PU. The difference can be ascribed to the hydrophilicity of the aliphatic or aromatic groups connected to the urethane moieties at the terminals of PUs.

Introduction

In order to construct a sustainable society, the chemical recycling of polymeric materials remains an extremely crucial issue to tackle. Polyurethanes are industrially important polymeric materials, which are used for a variety of applications, such as foams and elastomers.[1]   Some polyurethanes are responsible to external stimulus, and can be recycled owing to the reversible scission of covalent bonds within the structures.[2-4] Moreover, the hydrolysis of polyurethanes has been studied as a methodology for chemical recycling. However, polyurethanes obtained from alkanediols and diisocyanates are chemically stable polymers resistant to solvents. Several studies on the chemical recycling of polymers into monomers have been reported. It has been reported that the conversion to the desired monomers should proceed with high selectivity and utilize easy techniques by employing non-hazardous chemicals for the decomposition.

Degradation reactions[5-7] (e.g., hydrolysis, aminolysis, alcoholysis, and glycolysis) have been used for the chemical recycling of polyurethanes. However, the urethane linkages are relatively stable, and in some cases, protecting groups such as the benzoxycarbonyl group (Cbz) are used to mask their amino functionalities.[8] Therefore, a strong acid or base catalyst must be used for the hydrolysis.[9,10] Under such harsh

reaction conditions, excessive or unexpected degradation usually accompanies the solvolysis of polyurethanes; thus, the resulting reaction mixture may contain undesired byproducts in addition to the hydrolyzed products, i.e., alcohol and amine.[5,6]

In order to achieve satisfactory chemical recycling, the development of suitable catalysts for the hydrolysis of polyurethanes is desirable. Such catalysts should be safe, cheap, abundant, readily available, and easily removable from the reaction mixture. Furthermore, an appropriate catalytic activity may prevent the aforementioned excessive degradation of the hydrolyzed products.

Recently, a catalytic system using CO_2 in water, especially under high pressure, has received much attention since CO_2 and water are chemically safe and environmentally benign components. In this system, CO_2 produces carbonic acid *in situ* by reaction with water;[11,12] then, the formed carbonic acid acts as an acid catalyst.[13] Hydrolysis[14-17], reduction[12], and dehydration[18] reactions in the presence of this catalytic system have been already reported.

Previously, we have applied this hydrolysis system to an aromatic polyurethane (M-PU)[17] (Scheme 1). In this hydrolysis reaction, the formed carbonic acid effectively functioned as an acid catalyst to hydrolyze M-PU. Besides, this hydrolysis reaction produced the corresponding raw chemicals, diamine and diol, derived from the cleavage

of the repeating units of M-PU in excellent yields. A plausible reaction mechanism was discussed in a previous study,[17] according to which the acid activated the carbonyl group and then the hydrolytic cleavage of the urethane group occurred. For this process to occur, it is important that this chemical recycling system should include only CO_2 and water, and the concentration of the aqueous solution in the hydrolyzed reaction mixture allows to easily afford the raw chemicals with no need of neutralization or extraction.

The susceptibility of M-PU to hydrolysis depends on two major factors: (1) the inherent stability of the urethane groups under the reaction conditions, and (2) the accessibility of water to these linkages. The latter is expected to be affected by the hydrophilicity of the chemical structure around the urethane moieties. It was found that the urethane groups near the hydrophilic hydroxy groups at the polymeric terminals were more hydrolyzable than those next to the hydrophobic aminophenyl moieties. This result suggested that the chemical structure of PUs affected the hydrolyzability. Hence, it is important to clarify whether this hydrolysis system using CO_2 and water is applicable to other types of PUs consisting of aliphatic structures or not. Thus, the hydrolysis behavior of aromatic[17] and aliphatic PUs should be studied while paying attention to the relationship between the hydrolyzability and hydrophilicity dependent on the structure.

In this study, we investigated the hydrolytic behavior of aliphatic PUs bearing linear alkyl or bulky alicyclic moieties at the hard segments. These PUs were synthesized starting from 1,4-butanediol (BD) and aliphatic diisocyanates, 1,6-hexamethylene diisocyanate (HDI), or isophorone diisocyanate (IPDI). The hydrolysis was carried out in an aqueous solution under sub- or super-critical CO_2 conditions (below and above 7.1 MPa).

EXPERIMENTAL

Chemicals. Isophorone diisocyanate (IPDI), 1,4-butanediol (BD), methanol, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO) were purchased from WAKO Chemicals Co., Ltd., Osaka, Japan. 1,6-Hexamethylene diisocyanate (HDI) was kindly supplied by Nippon Polyurethane Industry Co., Ltd., Yamaguchi, Japan. HDI and IPDI were used after distillation under reduced pressure. BD and DMF were distilled over calcium hydride prior to use in polyaddition reactions. For the identification of the hydrolyzed products, authentic samples of isophorone diamine (I-DA) and hexamethylene diamine (H-DA) were purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. Other chemicals were commercially available as reagent grade and used as received unless otherwise stated.

Characterization. Fourier transform infrared (FT-IR) spectra were recorded on a Bio-Rad Laboratories FTS 3000 MXN spectrometer at room temperature. The transmission spectra were measured using a KBr disk at the resolution of 4 cm^{-1} in the wavenumber range of 4000-800 cm^{-1} with 32 scan times. ^{1}H-NMR spectra (400 MHz) were recorded on a JNM-GX400 spectrometer (JEOL Co. Ltd., Tokyo, Japan) using

tetramethylsilane (TMS) as an internal standard in chloroform-*d*, and measured at room temperature with 8-16 scan times. The 5% weight loss temperature (T_{d5}) was measured using a RIGAKU Thermos Plus TG8120 (Rigaku Denki, Co. Ltd., Japan) from room temperature to 500 °C with a heating rate of 10 K min^{-1} under a nitrogen atmosphere (flow rate of 50 mL min^{-1}). Elemental analysis (EA) was performed with a PerkinElmer 240II analyzer.

The number- and weight-average molecular weights (M_n and M_w, respectively) as well as the polydispersity index (PDI, M_w/M_n) were estimated by gel permeation chromatography (GPC) on a polystyrene gel column (Shimadzu Shim-pack GPC-802) using a Shimadzu HPLC 20AD pump system equipped with a refractive index detector using DMF as eluent at a flow rate of 1.0 mL min^{-1}. M_n, M_w and PDI were calibrated by polystyrene standards.

Preparation of polyurethanes (H-PU and I-PU). To a solution of BD (6.8 g, 76.3 mmol) in dry DMF (50 mL), HDI (12.6 g, 74.8 mmol) was added at 80 °C, and a white solid precipitated within 30 min. The reaction mixture was then stirred for 1 h. The consumption of the isocyanate groups was monitored by titration with dibutylamine.[19] A white solid precipitated from this solution, and it was separated from the reaction

mixture by filtration. The obtained precipitate was washed with methanol using a Soxhlet extractor, and it was then dried *in vacuo* to give H-PU as a white solid (18.9 g, 97.4%). The yield was calculated from the weight of H-PU and sum of both monomers. IR(KBr): 3321, 1685, 1535, 1263, and 1064 cm^{-1}. EA Calcd. for $C_{12}H_{22}N_2O_4$: C, 55.80; H, 8.58; N, 10.84; Found: C, 55.64; H, 8.72; N, 10.73. $T_{d5} = 282$ °C.

The reaction between IPDI and BD gave I-PU according to a similar procedure as that used for the synthesis of H-PU. The viscosity of the reaction mixture increased with the elongation of the reaction time without precipitation. After cooling, the reaction mixture was poured into a large amount of methanol to afford a white solid. The obtained white solid was reprecipitated with methanol, and dried *in vacuo* to give a I-PU as a white solid (96.7%). The ^{1}H-NMR and IR spectra are shown in Figures 1S and 2S, ESI.

IR(KBr): 3451, 3335, 2954, 1634, 1546, and 1251 cm^{-1}. EA Calcd. for $C_{16}H_{28}N_2O_4$: C, 61.51; H, 9.03; N, 8.97; Found: C, 61.47; H, 9.19; N, 9.03. $T_{d5} = 204$ °C.

General procedure for the hydrolysis of PUs.[17] First, 0.50 g of H-PU and 20 mL of water were placed into a 200 mL stainless autoclave equipped with a pressure gauge followed by the introduction of an appropriate amount of liquid CO_2. Then, the

autoclave was heated using a band heater under a high pressure of CO_2 (8.0 MPa). After

2 h, the reactor was rapidly immersed into an ice bath to cool to room temperature. Then,

a valve of the reactor was opened to release the pressured CO_2. Finally, the reaction

mixture was collected from the reactor and separated into a filtrate and water insoluble

residue (WIR) using a filter paper. The obtained WIR was washed with water and

methanol before being dried under vacuum at 60 °C for 24 h, and eventually weighed.

Under these reaction conditions, 0.28 g of WIR was obtained.

The degree of hydrolysis of PUs was estimated from the following equations:[17]

W_0 = Weight of starting PU

W_{WIR} = Weight of WIR

Degree of hydrolysis (%) = ((W_0 - W_{WIR}) / W_0) × 100

The degree of hydrolysis under the employed conditions (8.0 MPa CO_2 at

190 °C for 2 h) was calculated from the weights (0.28 g W_{WIR} and 0.50 g W_0) to be 44%.

The obtained WIR was analyzed by FT-IR spectroscopy.

The filtrate was concentrated in a rotary evaporator to afford an oil-containing

solid (0.21 g), which was weighed after drying. The water-soluble oil-containing solid

obtained from the filtrate was analyzed by ^{1}H-NMR spectroscopy in chloroform-*d*.

In order to clarify the effect of the reaction conditions, the hydrolysis was carried out upon changing single parameters such as the reaction time, CO_2 pressure, or reaction temperature. In all reactions, 20 mL of water and 0.50 g of PU were used.

RESULTS AND DISCUSSION

Preparation of polyurethanes (H-PU and I-PU)

Scheme 2 shows the preparation route to produce two types of aliphatic polyurethanes (PUs), namely poly(1,4-tetramethylene 1,6-hexamethylene dicarbamate) and poly(1,4-tetramethylene 1,3,3-trimethylcyclohexane 1-methylene-5-dicarbamate), abbreviated as H-PU and I-PU, respectively. The PUs were obtained by the polyaddition reactions of the corresponding diisocyanate (DI) and 1,4-butanediol (BD) with a molar ratio of $[BD]_0/[DI]_0 = 1.02$. A small excess of BD was used for the synthesis of H-, I-PU bearing hydroxy groups at the terminal units. After the reaction, the consumption of the isocyanate groups was confirmed by titration with dibutylamine.[19] The obtained PUs were characterized by FT-IR and elemental analyses. The 5% weight loss temperatures (T_{d5}) of H-PU and I-PU were 282 and 204 °C, respectively, as determined by the TG analysis. H-PU was found to be insoluble in common solvents, such as DMF, DMAc, DMSO, methanol, ethanol, toluene, chloroform, hexane, and ethyl acetate. H-PU was previously synthesized by other researchers and described to be soluble in common solvents.[20,21] On the contrary, Ambrožič and co-workers reported that H-PU has a poor solubility.[22] This difference in solubility might be due to the molecular weight of H-PU.

I-PU was insoluble in some solvents (i.e., methanol, hexane, ethyl acetate, and

water), while dissolving in DMF, DMAc, DMSO, and chloroform. As a reference, an aromatic PU (poly(methylene bis-(1,4-phenylene)hexamethylene dicarbamate: M-PU[17]) was found to be soluble in polar solvents, as detailed in a previous study.

Hydrolysis reaction of PU and identification of the reaction products

It has been reported that the pH values of aqueous carbonic acid solutions depend on the CO_2 pressure and temperature.[11, 23-26] By judging from a representative study,[25] under our conditions of 8.0 MPa CO_2 at 190 °C, the pH value is expected to be around 3.5-4.0.

Firstly, the hydrolysis of H-PU (0.50 g) in water under typical conditions (8 MPa CO_2, 190 °C, 2 h) was carried out. A water insoluble residue (WIR) of 0.28 g and a filtrate containing the water-soluble parts of 0.21 g (after drying) were obtained. Obviously, the weight of H-PU decreased after the hydrolysis reaction.

Figure 1 shows the FT-IR spectra of H-PU and WIR. In the spectrum of H-PU, the absorbance bands at 3321, 1685, 1535, 1263, and 1064 cm^{-1} were assigned to ν(N-H)$_{H-bond}$, ν(C=O)$_{H-bond}$, ν(C-N) with (N-H), ν(C-O), and ν(O=C-O-C), respectively.[22, 27] The absorption bands observed in the FT-IR spectrum of WIR were

identical to those of H-PU. These experimental data suggested that the WIR had the same repeating structure as H-PU, and no side reaction occurred at the main chain upon hydrolysis. These results matched those of the hydrolysis of M-PU, as previously reported.[17]

On the other hand, the obtained oil-containing solid was found to be soluble in common solvents, such as DMF, DMAc, DMSO, methanol, ethanol, and chloroform; thus, it was characterized by ^{1}H-NMR analysis in chloroform-*d*. Figure 2 shows the spectrum of the oil-containing solid without purification. The observed signals *A* and *B* at 3.62 and 1.65 ppm were assigned to a set of protons due to BD. Similarly, the signals *a* at 2.70 ppm, *b* at 1.45 ppm, and *c* at 1.33 ppm were ascribed to a set of protons due to 1,6-hexamethylenediamine (H-DA). Both BD and H-DA in the spectra were assigned by comparison with the ^{1}H NMR analyses of commercially available authentic samples of BD and H-DA. Therefore, it was obvious that the obtained compound was a mixture of BD and H-DA, which are components of the repeating units of H-PU. Additionally, no other signals appeared in the ^{1}H-NMR spectrum of the solid.

Similarly, water-soluble compounds and a water insoluble residue (WIR$_I$) were obtained when I-PU was hydrolyzed under a high pressure of CO_2 in the presence of water.

The absorption bands in FT-IR spectra (SI, Figures S1 and S3) of WIR_I and

the original I-PU were observed at the same wavenumbers as in the spectra of the H-PU

series in Figure 1.

The M_n and PDI values of WIR_I and I-PU were also estimated on the basis of

GPC measurements (SI, Figure S5). The profile of WIR_I appeared bimodal, whereas

that of I-PU was unimodal. The two sets of (M_n, PDI) for WIR_I and I-PU were (3,500,

2.93) and (3,5000, 2.33), respectively. After the hydrolysis, the M_n value decreased,

while the PDI increased. The change in M_n and PDI was due to the hydrolytic cleavage

of the polymer chain during the reaction. This means that I-PU was hydrolyzed under

CO_2 in water to give WIR_I as the corresponding oligomer. The ^{1}H NMR spectra of

WIR_I and I-PU also exhibited similar patterns of the major signals (SI, Figures S2 and

S4). In addition, some new weak signals could be observed for WIR_I, which were

presumably attributable to the terminal units of the oligomeric I-PU. The appearance of

these signals can be well explained by the lowering of the molecular weights, as

supported by the GPC results of WIR_I. The water-soluble compounds obtained from

I-PU were a mixture of I-DA and BD (SI, Figure S6).

These results indicated that the hydrolysis of PUs under a high pressure of CO_2

proceeded with high selectivity affording raw chemicals. In a previous study about

M-PU[17], similar results were obtained from the hydrolysis reaction in this CO_2-water system to produce the corresponding raw chemicals, i.e., BD and 4,4'-methylenedianiline (M-DA).

Effect of the reaction time on the degree of hydrolysis of PUs

The effects of the reaction conditions were also evaluated in terms of the degree of PU hydrolysis.

The hydrolysis reaction of PUs was carried out at 190 °C under 8.0 MPa of CO_2 as a function of the reaction time. The corresponding results are shown in Figure 3. For comparison, three types of PUs were heated under a N_2 atmosphere of 8.0 MPa instead of CO_2 at the same temperature. As shown in Figure 3, the degree of hydrolysis under a N_2 atmosphere remained at low values (i.e., <3% for 24 h) over 29 or 44 h. This means that the hydrolysis of PUs barely takes place in the absence of a CO_2 atmosphere. Presumably, the aqueous solution was not acidic enough to hydrolyze PUs owing to the lack of protons deriving from the carbonic acid.

On the other hand, the reaction behavior dramatically changed under a CO_2 pressure, and the hydrolysis proceeded significantly, as illustrated in Figure 3. Upon high pressure CO_2 in water, 44% of H-PU was already hydrolyzed after 2 h.

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Surprisingly, this value increased to 98% after 24 h, suggesting that a quantitative hydrolysis was achieved without any additives such as nonvolatile acids. The hydrolysis of I-PU was carried out under the same conditions, and the hydrolysis proceeded up to 78 and 91% after conducting the reaction for 12 and 24 h, respectively. For both PUs, excellent degrees of hydrolysis were apparently achieved. As shown in Figure 3, the prolongation of the reaction time was effective for the hydrolysis of PUs. Moreover, no other chemicals were detected in the reaction mixture in all cases. It was concluded that the pressurization of CO_2 in water is essential for the hydrolysis of PUs. As a reference for the aliphatic PUs, the results of M-PU obtained in a previous work[17] are also shown in Figure 3, as well as the relationship between the hydrolysis and reaction time. Under these reaction conditions, the aliphatic PUs showed a higher degree of hydrolysis than the aromatic M-PU, and H-PU was more easily hydrolyzable than I-PU. It was evident that the degree of hydrolysis at a certain time followed the order H-PU > I-PU > M-PU[17] among the three PUs.

So far, Chapman et al. studied the hydrolysis of model polyurethane compounds under moderately acidic conditions.[28] In this report, the urethane moiety connected to an aliphatic alkyl group was more hydrolyzable than that connected to a phenyl group. The hydrolyzability observed in our study is in agreement with the results

of the model compounds.

Effect of the temperature on the degree of hydrolysis of PUs

In order to investigate the effect of the reaction temperature on the hydrolysis, the temperature was changed ranging from 90 to 190 °C. Figure 4 shows the relationship between temperature and degree of hydrolysis of PUs over 12 h under 8.0 MPa of CO_2. The data for M-PU are also shown in Figure 4.[17] At 190 °C, all PUs showed excellent degrees of hydrolysis. M-PU was scarcely hydrolyzed at 160 °C, and the degree of hydrolysis smoothly increased beyond 180 °C. The reason for this increase has been described in a previous report.[17] On the contrary, the relationship among the aliphatic PU samples was different from that of M-PU. I-PU showed a high degree of hydrolysis at lower temperatures than M-PU, which was 14 and 21% at 150 and 160 °C, respectively. Furthermore, H-PU started to be hydrolyzed already at 110 °C to provide a value of 8%.

It was reported that the pH values rise with increases in the temperatures of the CO_2-water system. For example, the reported pH values at 95 and 150 °C were 3.35 and 3.59 under 6.3 MPa CO_2,[25] suggesting that the acidic solution conditions became slightly milder with increasing temperatures. However, acid catalyzed reactions usually

proceed faster as the temperature increases.[16-18] It is expected that the pH increment has

a little effect on the hydrolysis compared with the high promotion of the reaction upon

increasing of the temperature.

Actually, the degree of hydrolysis of the three PUs gradually increased with

increases of the temperature. At the same temperature of 150 °C, the degree of

hydrolysis of H-PU, I-PU, and M-PU was found to be 25, 14, and 5%, respectively. The

hydrolyzability depended on the chemical structures of PUs, which differed in their

hydrophilicity. This hydrolyzability tendency was also observed in the time-dependence

of the degree of hydrolysis (Figure 3).

Pressure of CO_2

Figure 5 shows the relationship between the CO_2 pressure (2.0-16.1 MPa) and

the degree of hydrolysis of PUs at 190 °C for 2 h. The data for M-PU are also shown

based on a previous report.[17] The degree of hydrolysis of each PU increased upon

increasing of the pressure from 2 to 6 MPa. It reached a maximum value at around 6

MPa, which is below the critical pressure of CO_2 (7.1 MPa) at 190 °C. On the other

hand, over 6 MPa, the degree of hydrolysis remained almost constant at 34.9~38.9%

(for I-PU) and 31.5~35.0% (for M-PU).

Peng *et al*. reported that the pH of CO_2 saturated water at 150 °C decreased

from 4.11 to 3.59 while increasing the pressure from 1.0 to 6.3 MPa, and reached a

plateau beyond 6.3 MPa.[25]   This pH change was consistent with our results, according

to which the degree of hydrolysis increased until *ca*. 6 MPa, and remained constant

beyond 6 MPa. Over 6 MPa, the carbonic acid might reach saturation in water under

these conditions. The degree for I-PU was slightly higher than that for M-PU.

Obviously, H-PU was more readily hydrolyzed than I-PU and M-PU, especially in the

range from 4 to 16 MPa. This order of hydrolyzability can also be observed in Figures 2

and 3. A similar behavior dependent on the CO_2 pressure was observed for the

hydrolysis of polyurea in a CO_2-water system, as previously reported.[14-16]

Comparison of the hydrolyzability among PUs

In a previous report,[17] a plausible mechanism for this hydrolysis was proposed.

Thus, a proton generated from carbonic acid activates one of the carbonyl groups of a

urethane linkage, followed by the nucleophilic attack of water to the activated carbonyl

carbon to form an oxonium cationic intermediate. From this intermediate, amino and

hydroxy groups at the two terminals A and B (Scheme 3) could be formed through a

carbamic acid group by cleavage of the urethane group. As illustrated in Scheme 3, the

urethane groups at the terminals A and B could be further hydrolyzed to afford two

products, i.e., a diamine and diol, which correspond to H-DA (or I-DA) and BD, respectively, in this study.

DAs and BD were obtained as water-soluble components in the filtrate after the hydrolysis. The actual composition of [H-DA]:[BD] and [I-DA]:[BD] was estimated from the integral ratio of the signals in each ^{1}H-NMR spectrum. The value of [M-DA]:[BD] was also cited from a previous report,[17] in which M-DA was generated from M-PU. When the hydrolysis conditions of PUs were 8.0 MPa CO_2 at 190 °C for 2 h, the values of [H-DA]:[BD], [I-DA]:[BD], and [M-DA]:[BD] were 40.0:60.0, 32.7:67.3, and 17.9:82.1, respectively.

All samples hydrolyzed under variously examined conditions showed similar trends in the compositions, suggesting that (1) the water-soluble components were always rich in the ratio of BD, and (2) the ratios of [H-DA], [I-DA], and [M-DA] to [BD] decreased in this order. The former consideration (1) indicates that, as shown in Scheme 3, the hydrolysis rate (k_b) of the urethane moiety close to terminal B is faster than that (k_a) of the moiety close to terminal A, whereby the filtrate became rich in BD in analogy with a previous study.[17] The latter consideration (2) also indicates that different hydrophobic moieties (R in Scheme 3) such as alkyl, alicyclic, and aryl groups changed the rate k_a of the hydrolytic cleavage at terminal A, thus the urethane moiety

connected to H-DA was more easily hydrolyzed than those connected to I-DA and

M-DA. It can be expected that the difference in the hydrolytic behavior among these

three types of terminal A would arise from the hydrophilicity of the terminal moieties

containing the amino groups. Therefore, the urethane moiety connected to H-DA at the

terminal A is more hydrophilic than the others (connected to I-DA and M-DA), thus

being in contact with water that causes the hydrolysis. This hydration hypothesis is in

good agreement with the fact that the solubility of diamines, H-DA, I-DA, and M-DA in

water is high, following the order 800 (at 15.6 °C), 8.5 (at 20 °C), and 1.25 (at 16 °C) g

L^{-1} for H-DA[29], I-DA[30], and M-DA[31], respectively. Moreover, the increase of the ratio

of [H-DA], [I-DA], and [M-DA] in the filtrate is well supported by the obtained data

shown in Figures 2, 3, and 4, in which H-PU was hydrolyzed more easily, followed by

I-PU and M-PU.

CONCLUSION

In this study, two types of aliphatic PUs (H-PU and I-PU) were synthesized starting from 1,4-butanediol (BD) and diisocyanates (HDI or IPDI) possessing an *n*-hexyl group or a highly bulky cyclohexane ring. The hydrolysis reactions of PUs were carried out in a pressurized CO_2-water system. The reaction behavior was investigated by changing the temperature (90-190 °C), time (up to 52 h), and CO_2 pressure (2.0-16.1 MPa). It was found that the degree of hydrolysis of PUs increased with the temperature and time, mostly reaching a constant value over 6 MPa CO_2. H-PU started to be hydrolyzed under at a relatively low temperature of 110 °C. The maximum degree of hydrolysis obtained was 98 and 91% for H-PU and I-PU, respectively. As a result of the hydrolysis of the urethane linkages, both H-PU and I-PU successfully afforded the respective diol (BD) and diamines as water-soluble components within the reaction mixture. Both raw materials could be easily obtained by evaporation of the water-soluble layers. These trends were similar to the hydrolysis of an aromatic PU (M-PU) investigated in a previous study.[17] It was found that, among the three PUs, the fast rate of hydrolysis followed the order H-PU > I-PU> M-PU. The difference is probably due to the hydrophilicity around the urethane linkage in the polymer terminal moiety.

This efficient and environment-friendly hydrolytic system using CO_2 and water

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was applicable to various types of PUs, including aromatic and aliphatic derivatives. Moreover, this system might be valuable for the chemical recycling of condensation polymers as well as the industrial application of chain-extended and cross-linked polyurethanes.
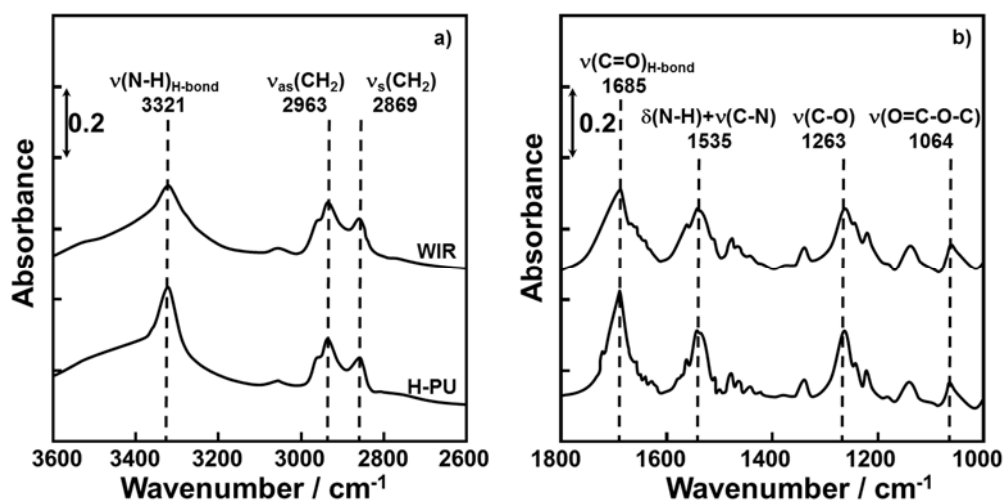
ACKNOWLEDGEMENTS

REFERENCES AND NOTES

1. Stenzenberger, H. D., Hummel, D. O. *Angew. Makromol. Chem.* **1979**, *82* (1), 103-127.

2. Zhang, L., Chen, L., Rowan, S. J. *Macromol. Chem. Phys.* **2017**, *218*, 1600320.

3. Zhang, L., Rowan, S. J. *Macromolecules* **2017**, *50*, 5051-5060.

4. Delebecq, E., Pascault, J.-P., Boutevin, B., Ganachaud, F. *Chem. Rev.* **2013**, *113*, 80-118.

5. Scheirs, J. In Polymer Recycling; Wiley: New York, **1998**; Chapter 10.

6. Zia, K. M., Bhatti, H. N., Bhatti, I. A. *React. Funct. Polym.* **2007**, *67*, 675-692.

7. Liu, L., Tang, L., Zhu, Z., Ni, Y., and Wu, Y. *Proceedings of MATEC Web of Conferences* **2016**, *64*, 02002.

8. Greene, T. W., Wuts, P. G. M. In Protective Groups in Organic Synthesis, 3rd ed., Wiley and Sons Inc., New York, 1999, Chapter 7.

9. Sato, K., Sumitani, K. (TEIJIN Limited) Jpn. Pat. 7,309,810, November 28,1995.

10. Ishihara, K., Ishida, K. (TEIJIN Limited) Jpn. Pat. 11,302,227, November 02, 1999.

11. Toews, K. L., Shroll, R. M., Wai, C. M., Smart, N. G. *Anal. Chem.* **1995**, *67*, 4040-4043.

12. West, K. V., Wheeler, C., McCarney, J. P., Griffith, K. N., Bush, D., Liotta, C. L., Eckert, C. A. *J. Phys. Chem. A.* **2001**, *105*, 3947-3948.

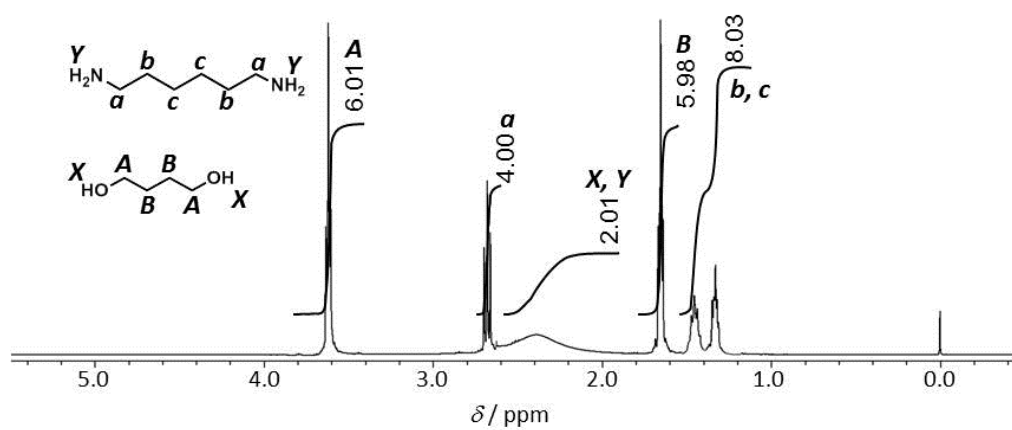13. Li, G., Jiang, H., Li, J. *Green Chem.* **2001**, *3*, 250-251.

14. Furukawa, M., Kojio, K., Motokucho, S. (Nippon Polyurethane Industry Co., Ltd.,) PCT pat. WO 2009130842, October 29, 2009.

15. Furukawa, M., Kojio, K., Motokucho, S. (Nippon Polyurethane Industry Co., Ltd.,) PCT pat. WO 2010125743, November 04, 2010.

16. Motokucho, S., Matsumoto, T., Nakayama, Y., Horiuchi, R., Morikawa, H., and Nakatani, H. *Polym. Bull.* **2017**, *74*, 615-623.

17. Motokucho, S., Yamaguchi, A., Nakayama, Y., Morikawa, H., Nakatani, H. *J. Polym. Sci. Part A: Poly. Chem.* **2017**, *55*, 2004-2010.

18. Motokucho, S., Morikawa, H., Nakatani, H., Noordover, B. A. J. *Tetrahedron Lett*. **2016**, *57*, 4742-4745.

19. Mayer, A. V. In Annual book of ASTM standards, **2010**, D5155.

20. Gartia, Y., Moore, J., Felton, C., Pulla, S., Berry, B., Munshi, P., Anindya, G. *J. App. Polym. Sci*. **2013**, *128*, 3522-3527.

21. Johnson, J. C., Wanasekara, N. D., Korley, L. T. J. *Biomacromolecules* **2012**, 1279−1286.

22. Ambrožič, G., Žigon, M. *Polym. Int*. **2005**, *54*, 606–613.

23. Roosen, C., Ansorge-Schumacher, M., Mang, T., Leitner, W., Greiner, L. *Green Chem*. **2007**, 9, 455-458.

24. Wang, X. X., Fu, H., Du, D. M., Zhou, Z. Y., Zhang, A. G., Su, C. F., Ma, K. F. *Chem. Phys. Lett*. **2008**, *460*, 339-342.

25. Peng, C., Crawshaw, J. P., Maitland, G. C., Trusler, J. P. M., Vege-Maza, D. *J. Supercrit. Fluids* **2013**, *82*, 129-137.

26. Pigaleva, M. A., Elmanovich, I. V., Koonevich, Y. N., Gallyamov, M. O., Muzafarov, A. M. *RSC Adv*. **2015**, *5*, 103573-103608.

27. Marin, R., Munoz-Guerra, S. *J. Polym. Sci. Part A: Poly. Chem.* **2008**, *46*, 7996-8012.

28. Chapman, T. M. *J. Polym. Sci. Part A: Poly. Chem.* **1989**, *27*, 1993-2005.

29. International programme on chemical safety, information data. http://www.inchem.org/documents/sids/sids/124094.pdf (accessed June 30, 2017)

30. International programme on chemical safety, information data. http://www.inchem.org/documents/sids/sids/2855132.pdf (accessed June 30, 2017)

31. International programme on chemical safety, information data. http://www.inchem.org/documents/sids/sids/101779.pdf (accessed June 30, 2017)

Figure 1. FT-IR spectra of H-PU (lower) and water insoluble residue (WIR) (upper) in the range of a) 2600-3600 and b) 1000-1800 cm^{-1}.

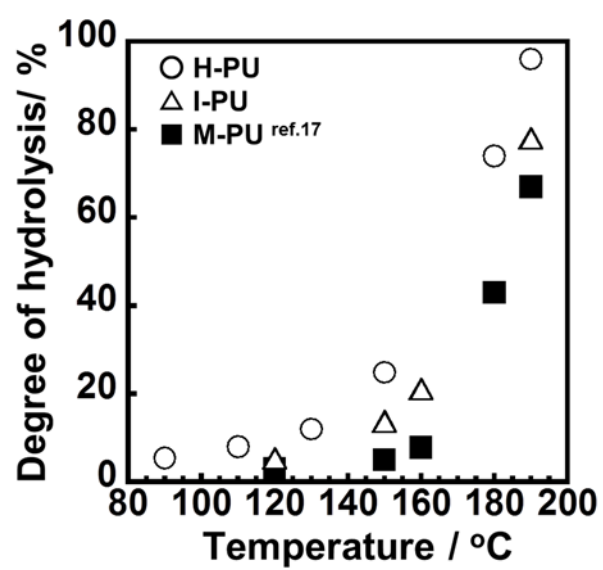**Figure 2**. ^{1}H-NMR spectrum of the filtrate as an oil-containing solid in chloroform-*d*.

Figure 3. Changes of the degree of hydrolysis with the reaction time at 190 °C under 8.0 MPa of CO_2 (open marks) and 8.0 MPa of N_2 (filled marks).

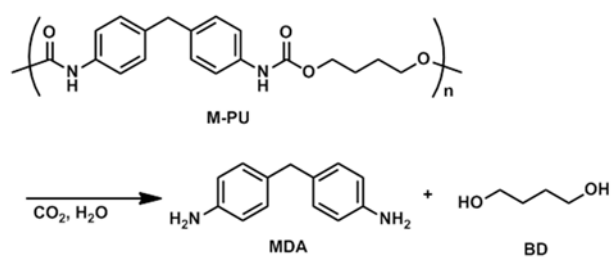**Figure 4**. Relationship between the reaction temperature and degree of hydrolysis of PUs over 12 h under 8.0 MPa of CO_2.
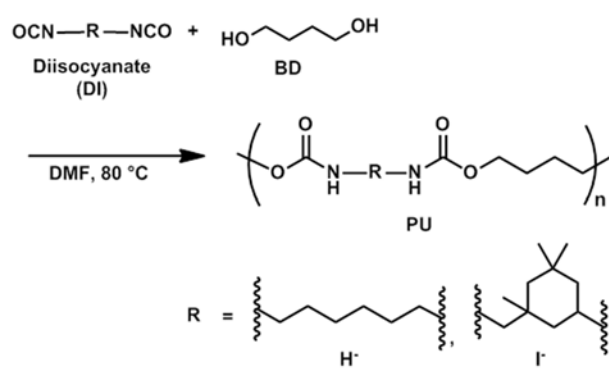
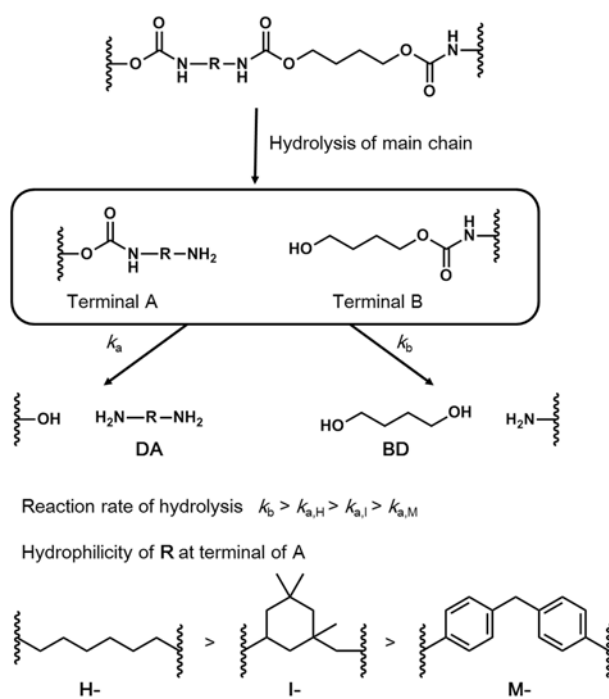**Figure 5**. Pressure dependence of the degree of hydrolysis of PUs at 190 °C over 2 h.

Scheme 1. Hydrolysis reaction of M-PU in the CO$_2$-water system.

M-PU

CO$_2$, H$_2$O

MDA

BD

Scheme 2. Preparation scheme of aliphatic polyurethanes H-PU and I-PU.

Scheme 3. Hydrolysis pathway of PUs.

CAPTIONS

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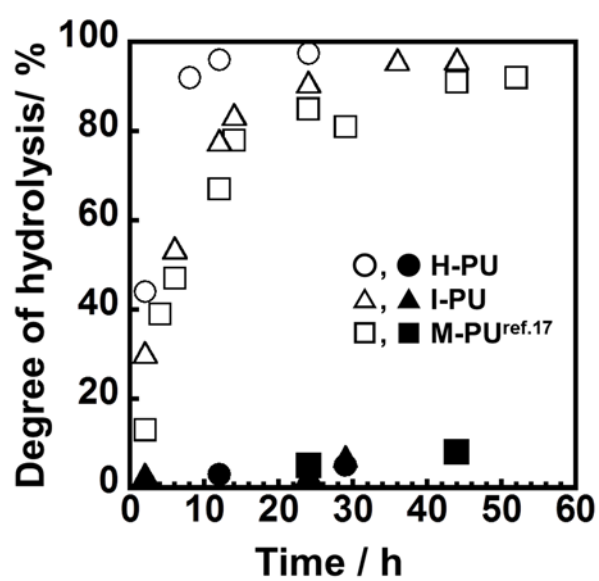
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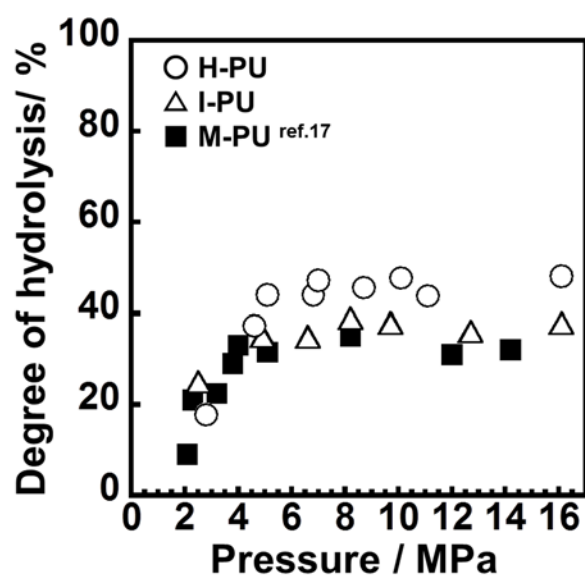
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